

FORM PTO-1390 (Modified) (REV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER 220640US0PCT	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 10/070424	
INTERNATIONAL APPLICATION NO. PCT/FR00/02519		INTERNATIONAL FILING DATE 13 September 2000		PRIORITY DATE CLAIMED 16 September 1999	
TITLE OF INVENTION A METHOD OF OBTAINING WATER-SOLUBLE POLYMERS, THE POLYMERS OBTAINED AND USES THEREOF					
APPLICANT(S) FOR DO/EO/US SUAU Jean-Marc et al.					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information: <ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below. 4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input checked="" type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). 10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)). 11. <input type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). 12. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210). <p>Items 13 to 20 below concern document(s) or information included:</p> <ol style="list-style-type: none"> 13. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 14. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 15. <input type="checkbox"/> A FIRST preliminary amendment. 16. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 17. <input type="checkbox"/> A substitute specification. 18. <input type="checkbox"/> A change of power of attorney and/or address letter. 19. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. 20. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 21. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 22. <input type="checkbox"/> Certificate of Mailing by Express Mail 23. <input type="checkbox"/> Other items or information: <p style="margin-left: 40px;"> Notice of Priority/PCT/IB/308 Drawings (1 sheet)/PCT/IB/304 Form PTO-1449 </p>					

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.492 (a)(1) - (5)) : <div style="font-size: 24pt; font-weight: bold;">10/070424</div>		INTERNATIONAL APPLICATION NO. <div style="font-weight: bold;">PCT/FR00/02519</div>		ATTORNEY'S DOCKET NUMBER <div style="font-weight: bold;">220640US0PCT</div>	
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24. The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : <div style="display: flex; justify-content: space-between;"> <div style="width: 80%;"> <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) </div> <div style="width: 15%; text-align: right;"> \$1040.00 \$890.00 \$740.00 \$710.00 \$100.00 </div> </div> <div style="text-align: right; font-weight: bold; margin-top: 10px;"> ENTER APPROPRIATE BASIC FEE AMOUNT = </div>				CALCULATIONS PTO USE ONLY <div style="border: 1px solid black; height: 100px; width: 100%;"></div>	
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30				<div style="border: 1px solid black; padding: 5px;">\$890.00</div> <div style="border: 1px solid black; padding: 5px;">\$130.00</div>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	- 20 =	0	x \$18.00	\$0.00	
Independent claims	- 3 =	0	x \$84.00	\$0.00	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$1,020.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				\$0.00	
SUBTOTAL =				\$1,020.00	
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30				\$0.00	
TOTAL NATIONAL FEE =				\$1,020.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL FEES ENCLOSED =				\$1,020.00	
				Amount to be refunded	\$
				charged	\$

a. ☒ A check in the amount of \$1,020.00 to cover the above fees is enclosed.


b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0030 A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.


NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:



22850


Surinder Sachar
Registration No. 34,423


 SIGNATURE

Norman F. Oblon
 NAME

24,618
 REGISTRATION NUMBER

March 18 2002
 DATE



22850

Surinder Sachar
Registration No. 34,423



UNITED STATES PATENT AND TRADEMARK OFFICE

Commissioner for Patents, Box PCT
United States Patent and Trademark Office
Washington, D.C. 20231
www.uspto.gov

U.S. APPLICATION NUMBER NO.	FIRST NAMED APPLICANT	ATTY. DOCKET NO.
10/070,424	Jean-Marc Suau	220640US0PCT

INTERNATIONAL APPLICATION NO.

PCT/FR00/02519

I.A. FILING DATE	PRIORITY DATE
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09/13/2000

09/16/1999

22850

OBLON SPIVAK MCCLELLAND MAIER & NEUSTADT PC
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1755 JEFFERSON DAVIS HIGHWAY
ARLINGTON, VA 22202

CONFIRMATION NO. 1485

371 FORMALITIES LETTER



OC000000008239704

Date Mailed: 06/07/2002

NOTIFICATION OF MISSING REQUIREMENTS UNDER 35 U.S.C. 371 IN THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)

The following items have been submitted by the applicant or the IB to the United States Patent and Trademark Office as an Elected Office (37 CFR 1.495):

- U.S. Basic National Fees
- Priority Document
- Copy of IPE Report
- Copy of references cited in ISR
- Copy of the International Application
- Copy of the International Search Report
- Information Disclosure Statements
- Request for Immediate Examination

RECEIVED: 6120
OBLON, SPIVAK, McCLELLAND
MAIER & NEUSTADT, P.C.

DOCKETING DEPT.

Initials/Date Docketed: 168120Type of Resp(s): Decl PubDue Date(s): 8-20

The following items **MUST** be furnished within the period set forth below in order to complete the requirements for acceptance under 35 U.S.C. 371:

- Oath or declaration of the inventors, in compliance with 37 CFR 1.497(a) and (b), identifying the application by the International application number and international filing date.

ALL OF THE ITEMS SET FORTH ABOVE MUST BE SUBMITTED WITHIN TWO (2) MONTH FROM THE DATE OF THIS NOTICE OR BY 22 or 32 MONTHS (where 37 CFR 1.495 applies) FROM THE PRIORITY DATE FOR THE APPLICATION, WHICHEVER IS LATER. FAILURE TO PROPERLY RESPOND WILL RESULT IN ABANDONMENT.

The time period set above may be extended by filing a petition and fee for extension of time under the provisions of 37 CFR 1.136(a).

Applicant is reminded that any communications to the United States Patent and Trademark Office must be mailed to the address given in the heading and include the U.S. application no. shown above (37 CFR 1.5)

A copy of this notice **MUST** be returned with the response.

DEBORAH D WILLIAMS

Telephone: (703) 305-3744

PART 1 - ATTORNEY/APPLICANT COPY

U.S. APPLICATION NUMBER NO.	INTERNATIONAL APPLICATION NO.	ATTY. DOCKET NO.
10/070,424	PCT/FR00/02519	220640US0PCT

FORM PCT/DO/EO/905 (371 Formalities Notice)

DOCKET NO.: 220640US0PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: Jean-Marc SUAUI et al.

SERIAL NUMBER: 10/070,424

FILED: March 18, 2002

FOR: A METHOD OF OBTAINING WATER-SOLUBLE POLYMERS, THE POLYMERS
OBTAINED AND USES THEREOF

RESPONSE TO NOTICE OF MISSING REQUIREMENTS UNDER 35 U.S.C. 371

ASSISTANT COMMISSIONER FOR PATENTS & TRADEMARKS
WASHINGTON, D.C. 20231

SIR:

Responsive to the notification dated 7 June 2002, and in accordance with the provisions of 35 U.S.C. 371, Applicants submit herewith a Rule 63 Declaration and a Preliminary Amendment. As a result of the Preliminary Amendment, no multiple dependencies remain in the claims. Accordingly, no additional claim fees are due.

The required surcharge was paid at the time of filing the application.

In light of the foregoing, this application is deemed to be in proper condition for examination and such favorable action is earnestly solicited.

Our check in the amount of \$162.00 is attached hereto. If any variance exists between the amount enclosed and the required Government fee, please charge or credit the difference to our Deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.

If these papers are not considered timely filed by the Patent and Trademark Office, then a petition is hereby made under 37 C.F.R. §1.136 and any additional fees required under 37 C.F.R. §1.136 for any necessary extension of time may be charged to Deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.



Norman F. Oblon
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10070424-073002



220640US-1835-1835-0-PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :
JEAN-MARC SUAUE ET AL : ATTN: APPLICATION DIVISION
SERIAL NO: 10/070424 :
FILED: MARCH 18, 2002 : EXAMINER:
FOR: A METHOD OF OBTAINING :
WATER-SOLUBLE POLYMERS,
THE POLYMERS OBTAINED AND
USES THEREOF

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows:

IN THE SPECIFICATION

Please replace the title on page 1, lines 1-2, with the following title:

METHOD FOR OBTAINING WATER-SOLUBLE POLYMERS,
RESULTING POLYMERS AND USES THEREOF.

IN THE CLAIMS

Please cancel Claims 13-18 and 20.

Please amend the claims as shown in the marked-up copy following this amendment to read as follows:

4. (Amended) A method of obtaining homopolymers and/or copolymers according to Claim 1, wherein the required quantity used of phosphorous acid and/or its salts or of sodium hypophosphite is greater than or equal to 0.5% by weight with respect to the total mass of the monomer or monomers.

5. (Amended) A method of obtaining homopolymers and/or copolymers according to Claim 1, wherein the sodium hydroxide, potassium hydroxide or lithium hydroxide are added in the form of a solution, in the form of a powder or in the form of pellets.

6. (Amended) A method of obtaining homopolymers and/or copolymers according to Claim 1, wherein the calcium hydroxide, calcium oxide, magnesium hydroxide or magnesium oxide are added in the form of a suspension, in the form of a powder or in the form of the salts of the corresponding anionic monomers.

7. (Amended) A method of obtaining homopolymers and/or copolymers according to Claim 1, wherein the ethylenically unsaturated monomer or monomers is at least one ethylenically unsaturated anionic comonomer.

8. (Amended) A method of obtaining homopolymers according to Claim 7, wherein the ethylenically unsaturated monomer is acrylic acid.

9. (Amended) A polymer in aqueous solution obtained by the method according to Claim 1, wherein the degree of neutralisation of the active acid sites is between 40% and 90%, limits included, for the sodium, potassium or lithium ions and between 10% and 60%, limits included, for the calcium and magnesium ions.

10. (Amended) A polymer in aqueous solution according to Claim 9, wherein said polymer is in the completely neutralised form.

11. (Amended) A polymer in aqueous solution according to Claim 9, wherein said polymer is partially neutralised.

12. (Amended) A polymer in aqueous solution according to Claim 9, wherein said polymer has a molecular weight in Mw weight of between 2000 and 16,000 determined by aqueous GPC whose standards, used as references, belong to a series of sodium polyacrylates sold by the company Polymer Standards Service under the names PSS-PAA varying from 18K to 2K.

19. (Amended) Aqueous suspensions of mineral materials containing the polymer according to Claim 9.

Please add the following new claims:

21. (New) A process for grinding one or more minerals, said process comprising grinding one or more minerals in an aqueous medium in the presence of the polymer solution of Claim 9.

22. (New) A process for dispersing one or more mineral materials, said process comprising

dispersing one or more mineral materials in an aqueous medium with the polymer solution of Claim 9.

23. (New) A process for making paper, said process comprising mixing the polymer solution of Claim 9 with a paper formulation, wherein the polymer solution acts as a water retaining agent.

24. (New) A method of treating water, said method comprising

sequestering or inhibiting the precipitation and/or incrustation of minerals in an industrial or domestic water by mixing the polymer solution of Claim 9 with said water.

25. (New) A method for preventing scale or corrosion in the field of inverse osmosis and ultrafiltration, said method comprising

mixing the polymer solution of Claim 9 with a fluid.

26. (New) A method for treating a drilling fluid, said method comprising mixing the polymer solution of Claim 9 with said drilling fluid.

27. (New) A method for preventing or treating scale, said method comprising mixing the polymer solution of Claim 9 with a detergent formula to form a mixture, wherein said mixture has a stable chlorometric rate of one or more hypochlorides present in said detergent.

28. (New) A method for dispersing an agent, said method comprising mixing the polymer solution of Claim 9 with a detergent formula to form a mixture, and dispersing an agent with said mixture, wherein said mixture has a stable chlorometric rate of one or more hypochlorides present in said detergent.

29. (New) A method for stabilizing a zeolite, said method comprising mixing the polymer solution of Claim 9 with a detergent formula to form a mixture, and stabilizing a zeolite with said mixture, wherein said mixture has a stable chlorometric rate of one or more hypochlorides present in said detergent.

30. (New) A process for preparing an aqueous suspension of one or more mineral materials, said process comprising

mixing the polymer solution as claimed in Claim 9 with a paper, paint, ceramic, drilling fluid or detergent.

31. (New) The method of obtaining homopolymers and/or copolymers according to Claim 6, wherein the salts of the corresponding anionic monomers are selected from the group consisting of calcium acrylate, calcium methacrylate, magnesium acrylate, magnesium methacrylate and a mixture thereof.

32. (New) The method of obtaining homopolymers and/or copolymers according to Claim 7, wherein the ethylenically unsaturated anionic comonomer is selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, crotonic acid, fumaric acid, maleic anhydride, isocrotonic acid, aconitic acid, mesaconic acid, sinapinic acid, undecylenic acid, angelic acid, acrylamido methyl propanesulphonic acid, sodium methallylsulphonate and a mixture thereof.

33. (New) The method of obtaining homopolymers and/or copolymers according to Claim 1, wherein the ethylenically unsaturated comonomer is an ethylenically unsaturated non-ionic comonomer selected from the group consisting of acrylamide and methacrylamide.

34. (New) The method of obtaining homopolymers and/or copolymers according to Claim 32, wherein the ethylenically unsaturated comonomer is an ethylenically unsaturated non-ionic comonomer selected from the group consisting of acrylic acid and methacrylic acid

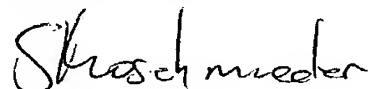
35. (New) The polymer in aqueous solution according to Claim 12, wherein said polymer has a molecular weight in Mw weight of between 3500 and 6500.

REMARKS

Claims 1-12, 19 and 21-35 are active in the present application. Claims 13-18 and 20 have been cancelled. Claims 1-12 and 19 have been amended to remove multiple dependencies and for clarity. Claims 21-35 are new claims. Support for the new claims is found in the original claims. No new matter is believed to have been added by this amendment. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.



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220640US-1835-1835-0-PCT

Marked-Up CopySerial No: 10/070,424

Amendment Filed on:

7-30-2002IN THE SPECIFICATION

Please replace the title on page 1, lines 1-2, with the following title:

--METHOD FOR OBTAINING WATER-SOLUBLE POLYMERS,
RESULTING POLYMERS AND USES THEREOF--.

IN THE CLAIMS

--4. (Amended) A method of obtaining homopolymers and/or copolymers according to [one of Claims 1 to 3, characterised in that] Claim 1, wherein the required quantity used of phosphorous acid and/or its salts or of sodium hypophosphite is greater than or equal to 0.5% by weight with respect to the total mass of the monomer or monomers.

5. (Amended) A method of obtaining homopolymers and/or copolymers according to [one of Claims 1 to 4, characterised in that] Claim 1, wherein the sodium hydroxide, potassium hydroxide or lithium hydroxide are added in the form of a solution, in the form of a powder or in the form of pellets.

6. (Amended) A method of obtaining homopolymers and/or copolymers according to [one of Claims 1 to 4, characterised in that] Claim 1, wherein the calcium hydroxide, calcium

oxide, magnesium hydroxide or magnesium oxide are added in the form of a suspension, in the form of a powder or in the form of the salts of the corresponding anionic monomers [such as calcium acrylate or methacrylate or magnesium acrylate or methacrylate].

7. (Amended) A method of obtaining homopolymers and/or copolymers according to [one of Claims 1 to 6, characterised in that] Claim 1, wherein the ethylenically unsaturated monomer or monomers is [or are chosen from amongst] at least one [of the] ethylenically unsaturated anionic comonomer [comonomers such as acrylic and/or methacrylic, itaconic, crotonic or fumaric acid, maleic anhydride or isocrotonic, aconitic, mesaconic, sinapinic, undecylenic or angelic acid, acrylamido methyl propanesulphonic acid or sodium methallylsulphonate and are optionally chosen from amongst the ethylenically unsaturated non-ionic comonomers such as acrylamide and/or methacrylamide, and preferentially chosen from amongst acrylic and/or methacrylic acid].

8. (Amended) A method of obtaining homopolymers according to Claim 7, [characterised in that] wherein the ethylenically unsaturated monomer is acrylic acid.

9. (Amended) A polymer in aqueous solution obtained by the method according to [any one of Claims 1 to 8, characterised in that] Claim 1, wherein the degree of neutralisation of the active acid sites is between 40% and 90%, limits included, for the sodium, potassium or lithium ions and between 10% and 60%, limits included, for the calcium and magnesium ions.

10. (Amended) A polymer in aqueous solution according to Claim 9, [characterised in that it] wherein said polymer is in the completely neutralised form.

11. (Amended) A polymer in aqueous solution according to Claim 9, [characterised in that it] wherein said polymer is partially neutralised.

12. (Amended) A polymer in aqueous solution according to [any one of Claims 9 to 11, characterised in that it] Claim 9, wherein said polymer has a molecular weight in Mw weight of between 2000 and 16,000, [preferentially between 3500 and 6500,] determined by aqueous GPC whose standards, used as references, belong to a series of sodium polyacrylates sold by the company Polymer Standards Service under the names PSS-PAA varying from 18K to 2K.

19. (Amended) Aqueous suspensions of mineral materials containing the polymer according to [any one of Claims 9 to 12] Claim 9.--

Claims 13-18 and 20 (Cancelled).

Claims 21-35 (New).

1/p812

**A METHOD OF OBTAINING WATER-SOLUBLE POLYMERS, THE POLYMERS
OBTAINED AND USES THEREOF**

The invention relates to a novel method of obtaining
5 homopolymers and/or copolymers, in an aqueous solution of
monoethylenically unsaturated monomers such as acrylic and/or
vinyl monomers, making it possible to obtain directly usable
polymers.

10 The invention also relates to the homopolymers and/or copolymers
obtained by the said method as well as their use as an aid to
the grinding and/or dispersion in aqueous solution of mineral
materials, or as a sequestering agent or mineral scale and/or
15 incrustation inhibitor in particular on the heat transfer
surfaces of industrial or domestic installations or as a
fluidising agent for aqueous solutions based on soft or saline
water normally used as drilling fluids in the fields of civil
engineering, building, public works, petroleum prospecting or
20 extraction or as a zeolite suspension stabiliser and as an
antiscaling agent or as a water retaining agent in the paper
making industry or also as builder or co-builder in detergent
compositions or finally as dispersant which does not destabilise
the chlorometric rate of the hypochlorite compositions in the
detergent formulations containing it.

25 Finally, the invention relates to the said aqueous solutions of
mineral materials which are stable over time and have a high
concentration of mineral materials as well as their use in the
field of paper, paint, detergent and cleaning formulations and
30 any other field using the said suspensions such as in particular
ceramics or drilling fluids.

For a long time already persons skilled in the art have known
various methods for homopolymerising in solution acrylic and/or

vinyl monomers such as in particular acrylic acid, methacrylic acid, maleic anhydride or acrylamide as well as for copolymerising, in solution in water, acrylic acid with other monoethylenically unsaturated monomers such as for example
5 maleic anhydride, itaconic acid, acrylamide or acrylamido methyl propanesulfonic acid.

Thus the patents FR 2 751 335, EP 0 405 818, EP 0 618 240, US 4,621,127 and EP 0 792 890 describe methods of polymerising
10 acrylic acid.

Likewise a person skilled in the art has available US patent 4 301 266, which describes a method of manufacturing acrylic acid polymers having the drawback of requiring the use of a solvent
15 of the isopropanol type and requiring work under pressure, and distillation in order to eliminate the solvent.

Finally, persons skilled in the art also know the patents FR 2 539 137, EP 0 542 644 or EP 0 516 656 teaching that
20 neutralisation of acrylic polymers with alkaline earths makes it possible to obtain agents for the grinding of calcium carbonate by the wet method, these suspensions being particularly stable over time.

25 However, all these polymerisation techniques well known to persons skilled in the art require a step of neutralisation of the polymer solution obtained in acid form or partially neutralised subsequently to the polymerisation reaction, then obliging the producer of these polymers either to equip himself
30 with equipment specific to the polymerisation and another type of equipment peculiar to the neutralisation reactions or to occupy the polymerisation reactors for a longer time, which has the consequence of reducing the productivity of the installation and therefore increasing the cost of the products.

Confronted with these various drawbacks, which cannot fully satisfy a person skilled in the art, the Applicant has found, surprisingly, that dispersing agents and/or high-efficiency grinding aids of mineral materials can be obtained by the polymerisation of acrylic acid and ethylenically unsaturated monomers using phosphorous acid and/or its salts or sodium hypophosphite provided that, during the polymerisation process, neutralisation agents consisting of alkaline earths are introduced into the reaction medium after the partial neutralisation of the monomer or monomers by means of an alkali ion such as in particular sodium, potassium or lithium or the like.

This particular reaction then makes it possible to obtain, in a single step (the polymerisation and neutralisation being simultaneous), a grinding aid and/or dispersing agent in aqueous suspension of mineral materials.

These aqueous suspensions of mineral particles have a high concentration of mineral materials and have a Brookfield viscosity which is low and stable over time, even without stirring.

This aim is achieved by virtue of the method according to the invention, that is to say using phosphorous acid and/or its salts or sodium hypophosphite and by neutralisation during the polymerisation of the ethylenically unsaturated monomers by continuously adding, first of all, bases such as sodium hydroxide, potassium hydroxide or lithium hydroxide and then alkaline earth bases such as calcium hydroxide, magnesium hydroxide, calcium oxide or magnesium oxide.

Thus one of the aims of the invention is the development of the said method making it possible to obtain polymers in solution in a single step.

5 Another aim of the invention is to provide a grinding aid and/or a dispersing agent in aqueous suspension of mineral materials making it possible to arrive at aqueous dispersions of mineral materials which have a high concentration of mineral material and have a Brookfield viscosity which is low and stable over
10 time, even without stirring.

In addition another aim of the invention is to provide a sequestering agent or antiscaling agent or mineral scale inhibitor and/or incrustation inhibitor when the molecular
15 weight of the said homopolymers and/or copolymers is sufficiently low to be suited to the said application.

In addition to these aims, an additional object of the invention is to obtain a fluidising agent for aqueous suspensions used as
20 drilling fluids or to develop a stabiliser for aqueous suspensions of zeolites as well as to obtain an antiscaling agent.

In addition, another aim of the invention relates to the mineral
25 aqueous suspensions obtained by the use of the said agents.

Finally, another aim of the invention relates to the use of these mineral aqueous suspensions in the fields of the filling and coating of paper as well as paint, ceramics, detergents and
30 drilling mud.

Thus the method according to the invention of obtaining homopolymers and/or copolymers, in aqueous solution, of ethylenically unsaturated monomers is characterised by the use

of phosphorous acid and/or its salts or sodium hypophosphite and by neutralisation during the polymerisation of the ethylenically unsaturated monomers by the continuous addition, first of all, of bases such as sodium hydroxide, potassium hydroxide or lithium hydroxide and then alkaline earth bases such as calcium hydroxide, calcium oxide, magnesium hydroxide or magnesium oxide.

The ethylenically unsaturated monomer or monomers is (are) chosen from amongst at least one of the ethylenically unsaturated anionic monomers or comonomers such as acrylic and/or methacrylic, itaconic, crotonic or fumaric acid, maleic anhydride or isocrotonic, aconitic, mesaconic, sinapinic, undecylenic or angelic acid, acrylamido methyl propanesulphonic acid (referred in the remainder of the description as AMPS) or sodium methallylsulphonate or possibly chosen from amongst the ethylenically unsaturated non-ionic comonomers such as acrylamide and/or methacrylamide.

The ethylenically unsaturated monomer or monomers is (are) preferentially chosen from amongst acrylic or methacrylic acid and, highly preferentially, the invention uses solely acrylic acid.

In the method according to the invention, the homopolymerisation or copolymerisation reaction, and whatever the ratio by weight of the monomers, is effected by the use of phosphorous acid and/or its salts or sodium hypophosphite in a quantity determined according to the molecular weight required for the polymer, possibly in the presence of all or some of the water necessary for obtaining a homogenous solution.

All or some of the quantity of the said phosphorous acid and/or its salts or of the said sodium hypophosphite can be introduced

completely at the bottom of the polymerisation tank or added throughout the polymerisation at the same time as the other additions.

- 5 These other additions, which can be chosen from amongst the polymerisation initiators well known to persons skilled in the art such as in particular hydrogen peroxide alone or in a mixture with metallic salts, for example iron or copper, tert-butyl hydroperoxide, or sodium or potassium persulphates, and
10 the like.

The total quantity of phosphorous acid and/or its salts or sodium hypophosphite used in the method according to the invention is greater than or equal to 0.5% by weight with
15 respect to the total mass of the monomer or monomers making up the polymer according to the invention.

In the method according to the invention, the bases used are chosen from amongst sodium hydroxide, potassium hydroxide or
20 lithium hydroxide.

They can be added in solution form but also in the form of pellets or in powder form.

- 25 The alkaline earth bases used are chosen from amongst calcium hydroxide, calcium oxide, magnesium hydroxide or magnesium oxide.

The latter can be added in suspension form or in the form of a
30 powder but also in the form of salts of the corresponding anionic monomers such as in particular in the form of calcium and/or magnesium acrylate or methacrylate.

It should also be noted that, in the method according to the invention, the molecular weight of the required copolymer is not only a function of the quantity of initiators used but also the level of phosphorus involved as well as the concentration of the medium.

The polymerizate obtained can also be processed by any known means in order to eliminate the water therefrom and isolate it in the form of a fine powder and to use it in this form.

According to a variant of the invention, the polymers in solution according to the invention obtained by the method according to the invention and intended to be used as a grinding aid and/or dispersing agent, as a sequestering agent or scale and/or incrustation inhibitor or as an agent for fluidising aqueous solutions such as drilling fluids or as a zeolite stabilising agent can subsequently be fractionated by fractionation means well known to persons skilled in the art.

The polymers according to the invention are characterised in that they are obtained by the method according to the invention.

In addition they are characterised in that the degree of neutralisation of the active acid sites is between 40% and 90%, limits included, for alkali ions such as sodium, potassium or lithium, and between 10% and 60%, limits included, for alkaline earth ions such as calcium and magnesium.

The homopolymers and/or copolymers intended to be used according to the invention as a dispersing agent and/or grinding aid or a fluidiser for drilling muds or as a stabiliser for zeolite suspensions in detergent compositions or generally have a molecular weight in terms of M_w weight between 2000 and 16,000, preferentially between 3500 and 6500, determined by aqueous GPC,

for which the standards, used as references, belong to a series of sodium polyacrylates sold by the company Polymer Standards Service under the names PSS-PAA varying from 18K to 2K.

5 Likewise, when the polymer and/or copolymer according to the invention, obtained by the method of the invention is used in the treatment of industrial and/or domestic water for the purpose of conferring for example antiscaling and anticorrosion effects on these media or is used in the field of reverse
10 osmosis and ultrafiltration for the purpose of sequestering the cations present, its molecular weight in terms of M_w weight is between 2000 and 10,000, determined according to the same GPC measuring method as described above.

15 In practice the operation of dispersing of the mineral substance to be dispersed consists of preparing under stirring an aqueous solution of the dispersion agent according to the invention into which there is introduced the mineral substance to be dispersed, which can have highly diverse origins, such as natural or
20 synthetic calcium carbonate, dolomites, calcium sulphate, titanium dioxide or lamellar pigments such as for example mica or kaolin, that is to say all the mineral substances which must be put in suspension and dispersed in order to be useable in applications as diversified as the coating of papers, the
25 pigmentation of paints, ceramics, drilling muds or detergents.

Likewise, in practice, the operation of grinding the mineral substance to be refined consists of grinding the mineral substance with a grinding body into very fine particles in an
30 aqueous medium containing the grinding agent. First of all an aqueous suspension of the mineral substance to be ground is formed, whose grains have an initial size of no more than 50 microns at the required concentration.

The grinding body with a granulometry advantageously between 0.20 and 4 millimetres is added to the suspension of the mineral substance to be ground. The grinding body is in general in the form of particles and materials as diverse as silicon dioxide, aluminium oxide, zirconium oxide or mixtures thereof, as well as high-hardness synthetic resins, steels or others. An example of a composition of such a grinding body is given by the patent FR 2 303 681, which describes grinding elements formed by 30 to 70% by weight zirconium oxide, 0.1 to 5% aluminium oxide and 5 to 20% silicon dioxide. The grinding body is preferably added to the suspension in a quantity such that the ratio by weight between this grinding material and the mineral material to be ground is at least 2/1, this ratio preferably being between the limits 3/1 and 5/1.

The mixture of the suspension and grinding body is then subjected to the mechanical action of stirring, such as the one which occurs in a conventional microelement grinder.

The grinding aid and/or dispersing agent according to the invention is also introduced into the mixture formed by the aqueous suspension of mineral substances and by the grinding body at the rate of 0.2 to 2% by weight of the dried fraction of the said polymers with respect to the dry mass of the mineral substance to be refined.

The time required for arriving at an excellent degree of fineness of the mineral substance after grinding varies according to the nature and quantity of the mineral substances to be ground, and according to the stirring mode used and the temperature of the medium during the grinding operation.

The scope and advantage of the invention will be perceived more clearly by means of the following examples, which are not limitative:

5 Example 1:

The purpose of this example is to illustrate the method, according to the invention, of obtaining acrylic acid homopolymers or copolymers by the addition, throughout the polymerisation reaction, of neutralisation agents commencing
10 with the base corresponding to the alkali ion.

To do this, in a polymerisation reactor previously heated and filled with a load composed of water, phosphorous acid and the required quantity of soda for neutralising this acid, or sodium
15 hypophosphite, the various following tests were carried out.

Test N° 1:

In a two-litre glass reactor equipped with stirring, a thermometer and a cooling system, a load referred to as a tank
20 bottom was prepared at room temperature, composed of 104 grams of water, 43.9 grams of soda at 50% and 45 grams of 97% phosphorous acid.

During the rise in temperature of the tank bottom, four loads to
25 be introduced during the polymerisation were prepared.

For this purpose, 450 grams of 100% acrylic acid were introduced into a first beaker, into a second beaker 25 grams of hydrogen peroxide at 130 volumes and 80 grams of water, into a third
30 beaker 350 grams of soda at 50% and finally into a fourth beaker 70 grams of calcium hydroxide and 180 grams of water.

The hydrogen peroxide and acrylic acid were added separately and continuously during the two hours of polymerisation.

The soda contained in the third beaker was added proportionally to the acrylic acid and continuously. When all the soda was introduced, the lime contained in the fourth beaker was in its turn added until the end of the introduction of the acrylic acid.

The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and calcium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 70% by sodium and 30% by calcium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 4400 determined according to the GPC method cited above.

Test N° 2:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 1 with the exception of the quantity of hydrogen peroxide, which was multiplied by 0.68.

The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and calcium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 70% by sodium and 30% by calcium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 5000 determined according to the GPC method cited above.

Test N° 3:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 1 with the exception of the quantity of hydrogen peroxide, which was multiplied by 0.60.

The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and calcium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 70% by sodium and 30% by calcium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 6200 determined according to the GPC method cited above.

Test N° 4:

10 This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 1 with the exception of the quantity of hydrogen peroxide, which was multiplied by 0.15.

15 The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and calcium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 70% by sodium and 30% by calcium. The molecular weight M_w of the polyacrylate
20 thus obtained according to the invention was equal to 7200 determined according to the GPC method cited above.

Test N° 5:

25 This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 1 with the exception of the quantity of phosphorous acid and the quantity of soda present in the tank bottom, which were multiplied by 0.84.

30 The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and calcium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 70% by sodium and 30% by calcium. The molecular weight M_w of the polyacrylate

thus obtained according to the invention was equal to 5500 determined according to the GPC method cited above.

Test N° 6:

5 This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 1 with the exception of the quantity of phosphorous acid which was multiplied by 1.10 and the quantity of soda present in the tank bottom, which was multiplied by 1.10.

10

The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and calcium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 70% by sodium and 30% by calcium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 3800 determined according to the GPC method cited above.

15

Test N° 7:

20 In a two-litre glass reactor equipped with stirring, a thermometer and a cooling system, a load referred to as a tank bottom was prepared at room temperature, composed of 104 grams of water, 43.9 grams of soda at 50% and 45 grams of 97% phosphorous acid.

25

During the rise in temperature of the tank bottom, five loads to be introduced during the polymerisation were prepared.

30

For this purpose, 450 grams of 100% acrylic acid were introduced into a first beaker, into a second beaker 15 grams of hydrogen peroxide at 130 volumes and 65 grams of water, into a third beaker 20 grams of sodium persulphate and 60 grams of water, into a fourth beaker 237 grams of soda at 50% and finally into a fifth beaker 226 grams of magnesium hydroxide at 40% in water.

The soda contained in the fourth beaker was added continuously during the first hour of polymerisation at the same time as the hydrogen peroxide whilst the magnesium hydroxide contained in the fifth was added continuously during the second hour of polymerisation at the same time as the persulphate solution. The acrylic acid was added continuously during the two hours.

The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and magnesium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 50% by sodium and 50% by magnesium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 3800 determined according to the GPC method cited above.

15

Test N° 8:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 7 with the exception of the use of a single catalyst, namely 20 grams of sodium persulphate in 120 grams of water.

The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and magnesium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 50% by sodium and 50% by magnesium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 8600 determined according to the GPC method cited above.

Test N° 9:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 7 with the exception of the quantity of sodium persulphate, diluted to 7% in water, which was multiplied by 0.30, and with

the exception of the quantity of hydrogen peroxide, diluted to 12% in water, which was multiplied by 0.66.

5 The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and magnesium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 50% by sodium and 50% by magnesium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal
10 to 10,000 determined according to the GPC method cited above.

Test N° 10:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 9
15 with the exception of the quantity of hydrogen peroxide, diluted to 12.5% in water, which was multiplied by 0.30.

The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and magnesium
20 polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 50% by sodium and 50% by magnesium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 12,600 determined according to the GPC method cited above.

25

Test N° 11:

In a two-litre glass reactor equipped with stirring, a thermometer and a cooling system, a load referred to as a tank bottom was prepared at room temperature, composed of 104 grams
30 of water and 11.3 grams of sodium hypophosphite crystallised with one molecule of water.

During the rise in temperature of the tank bottom, six loads to be introduced during the polymerisation were prepared.

For this purpose, 450 grams of 100% acrylic acid were introduced into a first beaker, into a second beaker 15 grams of hydrogen peroxide at 130 volumes and 65 grams of water, into a third beaker 10 grams of sodium persulphate and 70 grams of water, into a fourth beaker 237 grams of soda at 50%, into a fifth beaker 226 grams of 40% magnesium hydroxide in water and into a sixth beaker 33 grams of sodium hypophosphite crystallised with one molecule of water diluted in 40 grams of water.

The soda contained in the fourth beaker was added during the first hour of polymerisation at the same time as the hydrogen peroxide whilst the magnesium hydroxide contained in the fifth was added continuously during the second hour of polymerisation at the same time as the sodium persulphate.

The acrylic acid and sodium hypophosphite were added continuously and separately throughout the polymerisation.

The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and magnesium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 50% by sodium and 50% by magnesium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 2400 determined according to the GPC method cited above.

Test N° 12:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 11 except for the quantity of sodium hypophosphite in the tank bottom, which was multiplied by 0.59, and that added continuously, which was multiplied by 0.62. Finally, the initiator consisted solely of 20 grams of hydrogen peroxide at

130 volumes diluted in 140 grams of water. This solution was added continuously during the two hours of polymerisation.

5 The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and magnesium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 50% by sodium and 50% by magnesium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal
10 to 5500 determined according to the GPC method cited above.

Test N° 13:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test
15 N° 11 except for the quantity of sodium hypophosphite in the tank bottom, which was multiplied by 0.59, and that contained in the sixth beaker, which was multiplied by 0.62.

20 The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and magnesium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 50% by sodium and 50% by magnesium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal
25 to 6000 determined according to the GPC method cited above.

Test N° 14:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test
30 N° 11 except for the quantity of sodium hypophosphite in the tank bottom, which was multiplied by 0.40, and that contained in the sixth beaker, which was multiplied by 0.42.

The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and magnesium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 50% by sodium and 50% by magnesium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 8350 determined according to the GPC method cited above.

Test N° 15:

10 This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 11 except for the quantity of sodium hypophosphite in the tank bottom, which was multiplied by 3.98, and that contained in the sixth beaker, which was zero, and finally with the exception
15 of the quantity of hydrogen peroxide contained in the second beaker, which was multiplied by 0.66, and the quantity of sodium persulphate contained in the third beaker, which was multiplied by 0.60.

20 The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and magnesium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 50% by sodium and 50% by magnesium. The molecular weight M_w of the
25 polyacrylate thus obtained according to the invention was equal to 9700 determined according to the GPC method cited above.

Test N° 16:

30 This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 12 except for the quantity of soda used, which corresponded to a 40% neutralisation of the active acid sites and that of magnesium hydroxide, which corresponded to a neutralisation of 60% of the active acid sites.

The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and magnesium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 40% by sodium
5 and 60% by magnesium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 4300 determined according to the GPC method cited above.

Test N° 17:

10 This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 16 except for the quantity of magnesium hydroxide, which was multiplied by 0.416.

15 The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and magnesium polyacrylate partially neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 50% by sodium and 25% by magnesium. The molecular weight M_w of the
20 polyacrylate thus obtained according to the invention was equal to 5000 determined according to the GPC method cited above.

It should be noted in this test that, for measuring the molecular weight by GPC, the polymer was completely neutralised,
25 50% by the sodium and 50% by the magnesium.

Test N° 18:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test
30 N° 4, with the exception of the quantity of hydrogen peroxide, which was multiplied by 4.08, and with the exception of the quantity of soda used, which corresponded to an 80% neutralisation of the active acid sites, and that of calcium

hydroxide, which corresponded to a 20% neutralisation of the active acid sites.

5 The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and calcium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 80% by sodium and 20% by calcium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 6000
10 determined according to the GPC method cited above.

Test N° 19:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test
15 N° 12, with the exception of the quantity of calcium hydroxide used which corresponded to a neutralisation of 25% of the active acid sites and that of magnesium hydroxide, which corresponded to a neutralisation of 25% of the active acid sites, these two alkaline earth hydroxides being added during the second hour of
20 polymerisation.

The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium, magnesium and calcium polyacrylate totally neutralised in a ratio corresponding to a
25 neutralisation of the active acid sites equal to 50% by sodium, 25% by magnesium and 25% by calcium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 5730 determined according to the GPC method cited above.

30

Test N° 20:

In a two-litre glass reactor equipped with stirring, a thermometer and a cooling system, a load referred to as a tank bottom was prepared at room temperature, composed of 104 grams

of water, 43.9 grams of soda at 50% and 45 grams of 97% phosphorous acid.

During the rise in temperature of the tank bottom, five loads to be introduced during the polymerisation were prepared.

For this purpose, 225 grams of 100% acrylic acid were introduced into a first beaker, into a second beaker 15 grams of hydrogen peroxide at 130 volumes and 65 grams of water, into a third beaker 10 grams of sodium persulphate and 70 grams of water, into a fourth beaker 237 grams of soda at 50% and finally into a fifth beaker 233 grams of water and 225 grams of acrylic acid at 100% previously having reacted with 226 grams of magnesium hydroxide at 40% in water.

The soda contained in the fourth beaker was added continuously during the first hour of polymerisation at the same time as the hydrogen peroxide whilst the magnesium acrylate contained in the fifth was added continuously during the second hour of polymerisation at the same time as the persulphate.

The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and calcium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 50% by sodium and 50% by magnesium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 9500 determined according to the GPC method cited above.

30 Test N° 21:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 2, with the exception of the fact that the fourth beaker

contained 30% of the total quantity of acrylic acid and that the latter had previously reacted with lime.

5 The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a sodium and calcium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 70% by sodium and 30% by calcium. The molecular weight M_w of the polyacrylate thus obtained according to the invention was equal to 11,500
10 determined according to the GPC method cited above.

Test N° 22:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 1
15 with the exception of the first beaker, which contained 400 grams of acrylic acid at 100% and 50 grams of acrylamide, the third beaker, which contained 312 grams of soda at 50%, and finally the fourth beaker, which contained 63 grams of calcium hydroxide.

20 The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to an acrylic acid-acrylamide copolymer completely neutralised by the sodium ion and by the calcium ion in a ratio corresponding to a neutralisation of the
25 active acid sites equal to 70% by the sodium and 30% by the calcium. The molecular weight M_w of the copolymer thus obtained according to the invention was equal to 4200 determined according to the GPC method cited above.

30 Test N° 23:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 1 with the exception of the first beaker, which contained 400 grams of acrylic acid at 100% and 50 grams of AMPS, the third

beaker, which contained 331 grams of soda at 50%, and finally the fourth beaker, which contained 66 grams of calcium hydroxide.

- 5 The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to an acrylic acid-AMPS copolymer completely neutralised by the sodium ion and by the calcium ion in a ratio corresponding to a neutralisation of the active acid sites equal to 70% by the sodium and 30% by the calcium. The
10 molecular weight M_w of the copolymer thus obtained according to the invention was equal to 4600 determined according to the GPC method cited above.

Test N° 24:

- 15 This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N° 1 with the exception of the first beaker, which contained 400 grams of acrylic acid at 100% and 50 grams of methacrylic acid, the third beaker, which contained 343 grams of soda at 50%, and
20 finally the fourth beaker, which contained 68 grams of calcium hydroxide.

- The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to an acrylic acid-methacrylic
25 acid copolymer completely neutralised by the sodium ion and by the calcium ion in a ratio corresponding to a neutralisation of the active acid sites equal to 70% by the sodium and 30% by the calcium. The molecular weight M_w of the copolymer thus obtained according to the invention was equal to 4200 determined
30 according to the GPC method cited above.

Test N° 25:

This test was carried out with the same equipment, the same operating method and the same quantities of reagent as Test N°

3, with the exception of the soda, which was replaced by potassium hydroxide.

5 The polymerizate then obtained in a single step was an orangey-yellow solution corresponding to a potassium and calcium polyacrylate completely neutralised in a ratio corresponding to a neutralisation of the active acid sites equal to 70% by potassium and 30% by calcium. The molecular weight M_w of the copolymer thus obtained according to the invention was equal to
10 5500 determined according to the GPC method cited above.

Example 2:

This example relates to the preparation of a suspension of coarse calcium carbonate subjected to grinding in order to
15 refine it in a microparticular suspension. For this purpose, a suspension of coarse calcium carbonate was prepared from a natural calcium carbonate, using:

- for Test N° 26 illustrating the reference test, the calcium
20 carbonate was simply put in suspension in 25% water without the addition of a dispersant, a dispersion with a concentration of 76% dry matter being impossible to achieve;

- for Test N° 27 illustrating the invention, the polyacrylate of
25 Test N° 1 completely neutralised by the soda and calcium hydroxide in a ratio corresponding to a 70% sodium and 30% calcium neutralisation;

- for Test N° 28 illustrating the invention, the polyacrylate of
30 Test N° 2 completely neutralised by the soda and calcium hydroxide in a ratio corresponding to a 70% sodium and 30% calcium neutralisation;

- for Test N° 29 illustrating the invention, the polyacrylate of Test N° 3 completely neutralised by the soda and calcium hydroxide in a ratio corresponding to a 70% sodium and 30% calcium neutralisation;

5

- for Test N° 30 illustrating the invention, the polyacrylate of Test N° 4 completely neutralised by the soda and calcium hydroxide in a ratio corresponding to a 70% sodium and 30% calcium neutralisation;

10

- for Test N° 31 illustrating the invention, the polyacrylate of Test N° 5 completely neutralised by the soda and calcium hydroxide in a ratio corresponding to a 70% sodium and 30% calcium neutralisation;

15

- for Test N° 32 illustrating the invention, the polyacrylate of Test N° 6 completely neutralised by the soda and calcium hydroxide in a ratio corresponding to a 70% sodium and 30% calcium neutralisation;

20

- for Test N° 33 illustrating the invention, the polyacrylate of Test N° 7 completely neutralised by the soda and magnesium hydroxide in a ratio corresponding to a 50% sodium and 50% magnesium neutralisation;

25

- for Test N° 34 illustrating the invention, the polyacrylate of Test N° 8 completely neutralised by the soda and magnesium hydroxide in a ratio corresponding to a 50% sodium and 50% magnesium neutralisation;

30

- for Test N° 35 illustrating the invention, the polyacrylate of Test N° 9 completely neutralised by the soda and magnesium hydroxide in a ratio corresponding to a 50% sodium and 50% magnesium neutralisation;

- for Test N° 36 illustrating the invention, the polyacrylate of Test N° 10 completely neutralised by the soda and magnesium hydroxide in a ratio corresponding to a 50% sodium and 50% magnesium neutralisation;

5

- for Test N° 37 illustrating the invention, the polyacrylate of Test N° 11 completely neutralised by the soda and magnesium hydroxide in a ratio corresponding to a 50% sodium and 50% magnesium neutralisation;

10

- for Test N° 38 illustrating the invention, the polyacrylate of Test N° 12 completely neutralised by the soda and magnesium hydroxide in a ratio corresponding to a 50% sodium and 50% magnesium neutralisation;

15

- for Test N° 39 illustrating the invention, the polyacrylate of Test N° 13 completely neutralised by the soda and magnesium hydroxide in a ratio corresponding to a 50% sodium and 50% magnesium neutralisation;

20

- for Test N° 40 illustrating the invention, the polyacrylate of Test N° 14 completely neutralised by the soda and magnesium hydroxide in a ratio corresponding to a 50% sodium and 50% magnesium neutralisation;

25

- for Test N° 41 illustrating the invention, the polyacrylate of Test N° 15 completely neutralised by the soda and magnesium hydroxide in a ratio corresponding to a 50% sodium and 50% magnesium neutralisation;

30

- for Test N° 42 illustrating the invention, the polyacrylate of Test N° 16 completely neutralised by the soda and magnesium hydroxide in a ratio corresponding to a 40% sodium and 60% magnesium neutralisation;

- for Test N° 43 illustrating the invention, the polyacrylate of Test N° 17 partially neutralised by the soda and magnesium hydroxide in a ratio corresponding to a 50% sodium and 25% magnesium neutralisation;

5

- for Test N° 44 illustrating the invention, the polyacrylate of Test N° 18 completely neutralised by the soda and calcium hydroxide in a ratio corresponding to a 80% sodium and 20% calcium neutralisation;

10

- for Test N° 45 illustrating the invention, the polyacrylate of Test N° 19 completely neutralised by soda, magnesium hydroxide and calcium hydroxide in a ratio corresponding to a 50% sodium - 25% magnesium - 25% calcium neutralisation;

15

- for Test N° 46 illustrating the invention, the polyacrylate of Test N° 20 completely neutralised by the soda and magnesium hydroxide in a ratio corresponding to a 50% sodium and 50% magnesium neutralisation;

20

- for Test N° 47 illustrating the invention, the polyacrylate of Test N° 21 completely neutralised by the soda and calcium hydroxide in a ratio corresponding to a 70% sodium and 30% calcium neutralisation;

25

- for Test N° 48 illustrating the invention, the acrylic acid-acrylamide copolymer of Test N° 22 completely neutralised by the soda and calcium hydroxide in a ratio corresponding to a 70% sodium and 30% calcium neutralisation;

30

- for Test N° 49 illustrating the invention, the acrylic acid-AMPS copolymer of Test N° 23 completely neutralised by soda and calcium hydroxide in a ratio corresponding to a 70% sodium - 30% calcium neutralisation;

- for Test N° 50 illustrating the invention, the acrylic acid-methacrylic acid copolymer of Test N° 24 completely neutralised by soda and calcium hydroxide in a ratio corresponding to a 70% sodium - 30% calcium neutralisation;

5

- for Test N° 51 illustrating the invention, the polyacrylate of Test N° 25 completely neutralised by potash and calcium hydroxide in a ratio corresponding to a 70% potassium - 30% calcium neutralisation.

10

For each test, an aqueous solution was prepared from calcium carbonate coming from the Orgon (France) deposit, with a mean diameter of around 50 micrometres.

15 The aqueous suspension had a dry matter concentration of 76% by weight with respect to the total mass with the exception of the reference test, for which the suspension had a dry matter concentration of 25% by weight with respect to the total mass.

20 The grinding aid agent was introduced into this suspension in the quantities indicated in the following table, expressed as a percentage by dry weight with respect to the weight of dry calcium carbonate to be ground.

25 The suspension circulated in a grinder of the Dyno-Mill type with a fixed cylinder and rotating impeller, whose grinding body consisted of corundum balls with a diameter in the range from 0.6 millimetres to 1.0 millimetres.

30 The total volume occupied by the grinding body was 1150 cubic centimetres whilst its weight was 2900 g.

The grinding chamber had a volume of 1400 cubic centimetres.

The circumferential speed of the grinder was 10 metres per second.

5 The calcium carbonate suspension was recycled at the rate of 18 litres per hour.

The outlet of the Dyno-Mill grinder was provided with a 200 micron mesh separator for separating the suspension resulting from the grinding and the grinding body. The temperature during each grinding test was maintained at approximately 60°C.

10 At the end of the grinding (To), a sample of the pigmentary suspension was recovered in a flask. The granulometry of this suspension (% of the particles less than 1 micrometre) was measured by means of a Sedigraph 5100 granulometer from
15 Micromeritics.

The Brookfield viscosity of the suspension was measured by means of a Brookfield viscometer type RVT, at a temperature of 20°C and speeds of rotation of 10 revolutions per minute and 100
20 revolutions per minute with the appropriate spindle.

After a residence time of 8 days in the flask, the viscosity of the suspension was measured by introducing, into the unstirred flask, the appropriate spindle of the Brookfield viscometer type
25 RVT, at a temperature of 20°C and speeds of rotation of 10 revolutions per minute and 100 revolutions per minute (viscosity BS = before stirring).

The same viscosity measurements were also made once the flask
30 had been stirred and constitute the AS (after stirring) viscosity results.

All these experimental results are set out in Tables 1 and 1a below, which also indicate the consumption, as a percentage by

weight, of grinding-aid agent used for obtaining the granulometry indicated:

TABLEAU 1

TEST N°	DRY MATTER CONCENTRATION OF THE SUSPENSION	GRINDING-AID AGENT			GRANULOMET RY (% particles <1 µm)	BROOKFIELD VISCOSITY OF THE SUSPENSION (at 20°C in mPa.s)		
		Polymer Test N°	M _w	Consumption of agent as a dry/dry %		T0 10 rev/min – 100 rev/min	8 days BS 10 rev/min – 100 rev/min	8 days AS 10 rev/min – 100 rev/min
26	25	-	-	-	-	800-450	20,000-2500	1200-650
27	76	1	4400	1.27	80	1800-670	4555-1010	1860-680
28	76	2	5000	1.24	80	2090-660	7490-1370	2790-900
29	76	3	6200	1.26	80	1670-530	4555-1070	1880-685
30	76	4	7200	1.20	75.3	2300-775	6080-1210	1810-635
31	76	5	5500	1.30	80	2200-700	6000-1200	2000-700
32	76	6	3800	1.25	80	1900-690	5500-1100	1920-690
33	76	7	3800	1.26	76	1790-590	4400-1040	1400-460
34	76	8	8600	1.16	67	780-315	5600-1310	840-330
35	76	9	10,000	1.26	72	2680-860	11,800-1880	3230-1090
36	76	10	12,600	1.25	65	1550-580	16,800-2410	2240-790
37	76	11	2400	1.22	80	5055-1470	4660-3400	10,860-2500
38	76	12	5500	1.28	77	2200-750	6400-1900	5500-1545
39	76	13	6000	1.32	70	1230-500	6000-1200	1300-525

BS: Measurement of the viscosity before stirring of the suspension

AS: Measurement of the viscosity after stirring of the suspension

Test N° 26 is the reference test

Tests 27 to 39 relate to the invention

TABLEAU 1 Bis

TEST N°	DRY MATTER CONCENTRATION OF THE SUSPENSION	GRINDING-AID AGENT			GRANULOMETR Y (% particles <1 µm)	BROOKFIELD VISCOSITY OF THE SUSPENSION (at 20°C in mPa.s)		
		Polymer Test N°	M _w	Consumption of agent as a dry/dry %		T0 10 rev/min – 100 rev/min	8 days BS 10 rev/min – 100 rev/min	8 days AS 10 rev/min – 100 rev/min
40	76	14	8350	1.34	68	2410-820	15,500-2340	2400-900
41	76	15	9700	1.28	73	7000-1600	28,200-3600	16,400-2600
42	76	16	4300	1.40	72	3000-1100	9000-2700	4200-1200
43	76	17	5000	1.25	78	2500-830	7000-2500	3500-1000
44	76	18	6000	1.25	77	2600-800	7500-1500	2200-700
45	76	19	5730	1.12	80	3500-1000	7500-1500	3700-1150
46	76	20	9500	1.27	74	3080-930	11,080-1680	3100-1040
47	76	21	11,500	1.20	72	4600-1400	16,800-2150	2920-1075
48	76	22	4200	1.25	77	2200-800	6500-1300	2200-730
49	76	23	4600	1.25	80	1850-700	4700-1070	1930-710
50	76	24	4200	1.32	80	2500-750	7800-1800	2600-850
51	76	25	5500	1.15	80	5000-1500	12,000-3000	6800-1850

BS: Measurement of the viscosity before stirring of the suspension

AS: Measurement of the viscosity after stirring of the suspension

Tests 40 to 51 relate to the invention

A reading of Tables 1 and 1a show the efficacy of the polymers of the invention, obtained by the method according to the invention, as a grinding aid of an aqueous suspension of mineral materials with a high concentration of dry matter.

Example 3:

This example relates to the use of an aqueous suspension of calcium carbonate according to the invention in the field of paper. This example also relates to the use of polymers according to the invention as water retaining agent. For this purpose, different 100% calcium carbonate coating colors are prepared and are composed of:

- 100 parts, expressed as dry matter, of an aqueous suspension of calcium carbonate to be tested,
- 10 parts, expressed as dry matter, of a styrene-butadiene latex sold by Dow under the name "DL 950",
- 0.25 parts, expressed as dry matter, of co-binder sold by Coatex under the name Rheocoat™ 35.

The various following tests are carried out :

Test N° 52:

This test illustrates the prior art and implements a carbonate calcium suspension sold by Omya under the name Hydrocarb™ 90 OG.

Test N° 53:

This test illustrates the invention and implements a carbonate calcium suspension with the same above-cited granulometry and containing the same polymer as the invention of test N° 6.

For both tests, the water-retention of the coating colors is determined by the method described hereafter.

The paper coating color to be tested is subjected to a pressure of 100 psi (7 bars) in a standard cylinder, equipped with a surface of the filter paper type capable of allowing water to pass.

After 20 minutes, the volume of water collected is measured in ml.

The lower the volume of water collected at the end of 20 minutes, the better is the retention.

To do this, use is made of an "API Fluid Loss Measurement" filter press (Figure 1/1) from Baroïd, which is composed essentially of a clamp (1) provided with a clamping screw (2) for locking the three parts of the filter body (3).

This body (3) is composed of:

- a base (4) with a hole provided with a nozzle through which the filtrate flows. This base (4) supports a metallic sieve (5) with a mesh of 60 to 80, on which is placed the 90 mm diameter filter paper (6) (Whatman™ N° 50), the equivalent of which is the DURIEUX BLEU™ N° 3 type,
- a cylinder with an inside diameter of 76.2 mm and a height of 128 mm,

- a cover (7) provided with a compressed gas inlet, whose seal with the cylinder is provided by means of a flat joint (8), of the same type as those (9) placed on the base (4).

To use the filter press, the following are fitted in the following order:

- the joint (9) on the base (4)
- the sieve (5) on the joints (9)
- the filter paper (6) on the sieve (5)
- the second joint (10) on the filter paper (6)

and the cylinder is fitted on the base (4) before locking the bayonet system.

Then it is filled with the coating color to be tested (approximately 480 g up to 3 cm from the top of the cylinder) before placing the cover (7) on the cylinder, interposing a joint (8).

Then the assembly is placed in the clamp (1) and is locked by means of the clamping screw (2), and then a graduated tube (12) is arranged underneath the nozzle.

A pressure of 7 bars is applied, simultaneously triggering a chronometer.

After 20 minutes the volume of fluid collected in the test tube (12) is noted. The accuracy of the result obtained is ± 0.2 ml.

The results of the water-retention measurement obtained, according to the method described above in the description, are set out in Table 2 below.

The results of the measurements of Brookfield viscosity determined at 10 and 100 revolutions per minute at 25°C by means of a Brookfield viscometer type DV-1 equipped with the appropriate spindle also appear in Table 2.

TABLE 2:

Test n°		Prior art	Invention
		52	53
FORMULATIONS :			
<u>Pigments</u> :			
Calcium carbonate Hydrocarb™ 90 OG		100	100
Calcium carbonate according to the invention			
<u>Latex</u> :			
DL 950		10	10
<u>Coliants</u> :			
Rheocoat™ 35		0,25	0,25
Solid content (%)		66,2	66,2
pH		9	9
Brookfield viscosities (mPa.s)	10 rev/min	2 700	3 570
	100 rev/min	632	715
Water-retention API (ml)	Vol in 20 min	3,25	2,65

The reading of Table 2 shows the use of aqueous suspensions of mineral materials according to the invention in the field of paper as well as the use of polymers according to the invention as water retaining agent in the paper making industry.

Example 4 :

This example relates to the use of aqueous suspensions of mineral materials according to the invention in a water-based interior matt paint. For this purpose, the efficiency as a dispersant of the polymers of the invention contained in the aqueous suspensions of mineral materials of the invention implemented in a interior matt paint.

Thus, for the tests N° 54 and 55, 0.12% by dry weight of the tested dispersant relative to the total weight of a same water-based matt paint formula was added under agitation to a container which already held 144.5 g of water and 1 g of 28% ammonia.

After agitating for a few seconds, once the polymer to be tested has been added to the water containing ammonia, the other constituents of the said water-based matt paint were added in succession, these being:

- 2 g of a biocide, marketed by Troy under the name of MERGAL™ K6N
- 1 g of an anti-foaming agent marketed by Henkel under the name of NOPCO™ NDW
- 69 g of rutile titanium oxide marketed by Millenium under the name TIONA RL 68
- 311.4 g of natural calcium carbonate marketed by Omya under the name of DURCAL™ 5
- 204 g of natural calcium carbonate marketed by Omya under the name of HYDROCARB™
- 154.7 g of a styrene-acrylic binder in dispersion, marketed by Rhodia under the name of RHODOPAS™ DS 910
- 10 g of monoethylene glycol
- 10 g of coalescing agent marketed by Eastman Chemicals under the name TEXANOL

1.3 g of 28% ammonia
10.0 g of a thickening agent marketed by Coatex under the
name RHEO™ 3000
quantity to make up 1000 g - water.

The various tests are:

Test N° 54:

This test is the reference test and illustrates the prior art implementing a sodium polyacrylate marketed by Coatex under the name COATEX P50.

Tests N° 55:

This test illustrates the invention and implements the polymer of the invention of test N° 6.

For each of these tests, after agitating the aqueous composition made up in this way for a few minutes, the Brookfield viscosities of the different compositions are measured at 25°C and at 10 revolutions per minute and 100 revolutions per minute using a standard RVT Brookfield viscometer fitted with the requisite spindle.

The rheological stability of the formulae over time and in terms of temperature is determined by measuring the Brookfield viscosities at 10 revolutions per minute and 100 revolutions per minute and at 25°C of these same formulae after storing at ambient temperature without agitation for 24 hours and for one week.

All these results are set out in table 3 below:

TABLE 3

	TEST No	DISPERSANT DRY % WEIGHT	BROOKFIELD VISCOSITY OF THE PAINT		
			T = 0 10 rev/min - 100 rev/min (mPa.s)	T = 24 hours 10 rev/min - 100 rev/min (mPa.s)	T = 1 week, 25°C 10 rev/min - 100 rev/min (mPa.s)
Prior art	54	0,12	13700 - 3700	17000 - 4900	19400 - 5600
Invention	55	0,12	12600 - 3400	15900 - 4600	18200 - 5050

The reading of table 3 shows the use of aqueous suspensions of mineral materials according to the invention in the field of paint.

Example 5 :

The purpose of this example is to illustrate the use of the polymers of the invention as an anti-scaling agent in water treatment applications, by measuring the delay in the precipitation of alkaline earths and more specifically calcium carbonate contained in natural or artificial waters, saline or not, in the presence of the said polymers.

To this end, for each of the tests, town water containing 5 ppm by dry weight of each of the polymers to be tested is introduced into a one-litre flask provided with a coolant, with the exception of test No 56, which is the reference test and in which the town water does not contain any polymer.

Tests No 57 and 58 illustrate the invention using the copolymers produced from tests No 6 and 11 respectively.

This water is heated to boiling point and under reflux. At $t = 0$, i.e. when the first ring of bubbles (start of boiling) appears, a 20 ml test sample is taken. This water is immediately filtered on a 0.45 micron Millipore filter then transferred to a 100 ml beaker to be metered with EDTA. For this purpose, a MERCK indicator buffer tablet, reference 108430, 3 ml ammonia buffer, is inserted in the beaker and agitated with a magnetic bar before filtering the water. After a few seconds of agitation, the EDTA 5.10^{-3} M is tapped using a burette until it is clear green in colour. The TH (hydrotimetric

titre) obtained is calculated by Volume EDTA tapped $\times 2.5$
= TH in ° French (1 degree French = 10 mg expressed in
CaCo₃ per litre of water) and the value obtained is then
written TH 0. Similarly, samples are taken after 15 and
30 minutes of boiling. The TH values obtained are then
noted TH 15 and TH 30 minutes boiling and are set out in
table 4 below:

TABLE 4

	TEST No	ANTI-SCALING AGENT	TH 0	TH 15	TH 30
REFERENCE TEST	56	-	29,4	7,9	6,6
INVENTION	57	Polymer test No 6	29,5	20,1	15,8
INVENTION	58	Polymer test No 11	29,4	20,1	16,5

The efficiency of the polymers of the invention obtained using the method of the invention as an anti-scale agent can be seen from table No 4.

Example 6 :

This example relates to chlorinated alkaline formulae used, amongst other things, as a bleaching and disinfecting agent in detergents but could also relate to other bleaching agents commonly used in detergency.

More specifically, the purpose is to demonstrate the fact that the use of the polymers/of the invention as an anti-scale and dispersing agent in these formulae is not detrimental to the stability of a chlorinated alkaline composition in terms of a decrease in the chlorometric rate which would imply a loss in efficiency of the hypochlorite solution contained in the detergent compound.

In this case, for each test, 29.35 grams of bleach with a chlorometric rate of 36.96 and 15 grams of 50% soda are added under agitation to a 200 ml beaker containing 50.65 grams of water.

Once this mixture has homogenised, 5 grams of the polymer to be tested are added except in the case of test No 59, which is the reference test and to which no polymer is added.

After waiting for the mixture to cool, 10 ml of the said mixture are diluted in 100 ml of water.

After dilution, the hypochlorites present in 20 ml of the diluted chlorinated alkaline composition are metered.

The hypochlorites are metered using the Bunsen method based on the principle of oxidation of the iodide ions by the hypochlorite ions. The iodine thus released is titrated by a solution of 0.1 N sodium thiosulphate which enables the chlorometric rate of the chlorinated alkaline composition to

be derived by a process of calculation.

The chlorometric rate ($^{\circ}\text{CL}$) for the 20 ml test sample is worked out as follows:

$$^{\circ}\text{CL} = \frac{\text{Volume of sodium thiosulphate}}{20} \times 11.2$$

The value obtained for the reference test No 59 is then used as a reference value and represents 100% of hypochlorite present in the formula.

The different tests conducted are:

Test No 59:

Reference test with no polymer.

Test No 60:

Test illustrating the prior art using a sodium polyacrylate produced by any method of the prior art and having a molecular weight M_w equal to 5500.

Test No 61:

Test illustrating the invention and using the polymer of test No 2.

For each of these tests, the chlorometric rate is determined by the same metering method after 24 hours and 8 days.

The results in percentage residual hypochlorite as compared with the reference are set out in table 5 below:

TABLE 5

	TEST No	POLYMER	T0 (%)	24 hours (%)	8 days (%)
REFERENCE TEST	59	-	100	100	99,5
PRIOR ART	60	Sodium polyacrylate of $M_w = 5500$	100	98,4	90,6
INVENTION	61	Polymer of test No 2	100	99,5	95,0

A reading of Table 5 above shows the change in the chlorometric number of each of the solutions and illustrates the fact that the polymers according to the invention obtained by the method of the invention make it possible not to destabilise the chlorometric number of the chlorinated alkaline composition.

Example 7:

This example concerns the use of a polymer according to the invention in the field of ceramics.

For this purpose, tests are first of all carried out on the efficacy of the polymer as a clay dispersant for slip and then tests of efficacy as an agent for grinding the clays used in the field of ceramics.

Test of efficacy as a dispersant:

For this purpose, untreated water and the polymer according to the invention to be tested were weighed in a 500 ml beaker stirred by means of a 70 mm diameter blade. Then the clay was added in a shower and dispersion was carried out for 20 minutes at 1200 rev/min.

Raw materials	Quantity (g)
Untreated water	300.09
Polymer of Test No 6	1.538
Clay	200.00
Quantity of dispersant dry/dry	0.30%

The slip thus produced was transferred to a flow viscometer of the Lehmann viscometer type. A first viscosity measurement was carried out at time T_0 and then a second at time $T_{10 \text{ min}}$.

The flow times read were 27.4 secs for the measurement at time T_0 and 31.05 for the measurement at $T_{10 \text{ min}}$. Given that a polymer is acceptable when the flow time at T_0 is less than 30 and the time at $T_{10 \text{ min}}$ is less than 35, the polymer is perfectly usable for the dispersion of clay for slip.

Test of efficacy as a clay grinding agent:

In a 400 ml ceramic jar, 300 g of 16 mm diameter ceramic balls (that is to say approximately 35 balls) were weighed. Next the clay and then the untreated water and finally the polymer according to the invention were weighed. The jar was closed and was placed on the grinder. Next grinding was carried out for 10 minutes at 560 rev/min. The grinder was finally stopped and a Ford No 4 beaker was filled with the slip.

Raw materials	Quantity (g)
Clay	133.33
Untreated water	200.06
Polymer of Test No 6	1.367
Quantity of dispersant dry/dry	0.40%

The flow time was measured with the Ford No 4 beaker (T_0), the slip was kept and a second measurement was carried out at time $T_{5 \text{ min}}$. The flow time at T_0 was 22.5 secs and that at $T_{5 \text{ min}}$ was 26.7. Given that, in order to

be useable for grinding, the polymer must make it possible to obtain a slip with a flow time T_0 of less than 25 secs and an increase in the flow time at 5 min of less than 25% of the value at time T_0 , in order to allow complete and rapid discharge of industrial grinders. The polymer can therefore be used as a clay grinding agent for an application in ceramics.

Example 8:

This exemple concerns the use of a polymer according to the invention as thinning agent of a drilling fluid.

1) Operating method:

In a Hamilton Beach bowl, synthetic sea water was weighed. This was stirred using the Hamilton Beach and the different clays and powders were added in a shower, stirring for 10 minutes between each addition. The pH was adjusted to 10.5 using 50% sodium hydroxide. The polymer according to the invention to be tested was added and stirring was carried for a further 10 minutes. The pH was once again adjusted to 10.5 using 25% sodium hydroxide. The mud obtained was poured into a rolling cell and was placed in the temperature rolling oven and left to age for one night at 150°C with rolling (approximately 70 revolutions/minute).

2) Formulation:

Raw materials	Quantity (g)
Sea Water	375.9
Swelling clay	17.655
Filler clay	10.088
Barytes	277.5
Filtrate reducing agent	5.35
Polymer of Test No 16	7.5
Quantity of dispersant dry/dry	0.96%

After rolling, the cell was recooled, the mud was poured into a Hamilton Beach bowl and stirred for 3 mins. At the end of the stirring, the rheological parameters of the mud were measured by means of a Fann viscometer. The plastic viscosity (Vp) found was 30 mPa.s, the yield value (Yv) 16 and the 10 secs and 10 min gels were 3.5 and 8 mPa.s. The polymer according to the invention therefore makes it possible to obtain a correct viscosity of the mud (Vp) allowing easy pumping and a yield value enabling the cuttings to be well held in suspension. The slight increase in gel between 10 secs and 10 min allows easy resumption of pumping after a stoppage of the well.

Example 9:

This example concerns the use of a polymer according to the invention as a co-builder in detergents with a low phosphate level.

A detergent having the following dry composition was prepared by putting in a slurry and then atomising against the flow in an atomiser with a high-pressure injection head.

Composition:

Builder (sodium tripolyphosphate)	17
Co-Builder (polymer according to the invention to be tested)	8
Surfactant (n-docecylbenzenesulphonate)	18
Stabiliser (sodium metasilicate)	7
Stabiliser (magnesium silicate)	2
Bleaching agent (sodium perborate)	21
Bleaching activator	2
Filling agent (sodium sulphate)	25

The detergent was then used for washing a square of soiled cotton, under the following conditions:

Temperature changing from	25 to 65°C
Duration of washing cycle	45 min
Hardness of water .. 300 ppm in CaCO ₃ equivalent (Ca: Mg=2/1)	
Washing powder concentration	10 g/l

The efficacy of the polymer was measured by the mean whiteness (reflectance) of the piece of the cotton. The piece washed with a washing powder in which the polymer according to the invention is replaced by the filling agent gave a reflectance of 52% whilst with the polymer of test No 2 according to the invention the reflectance was 56%. This increase represents an increased whiteness afforded by the property which the polymer has to reduce the formation of alkaline-earth salts which are insoluble during washing.

CLAIMS

1. A method of obtaining homopolymers and/or copolymers, in aqueous solution, of ethylenically unsaturated monomers, characterised by the use of phosphorous acid and/or its salts or sodium hypophosphite and by the neutralisation during the polymerisation of the ethylenically unsaturated monomers by the continuous addition, first of all, of bases such as sodium hydroxide, potassium hydroxide or lithium hydroxide and then bases of alkaline earths such as calcium hydroxide, calcium oxide, magnesium hydroxide or magnesium oxide.
2. A method of obtaining homopolymers and/or copolymers according to Claim 1, characterised in that the total required quantity of phosphorous acid used is introduced before the start of the polymerisation as a load in the tank bottom of the polymerisation reactor.
3. A method of obtaining homopolymers and/or copolymers according to Claim 1, characterised in that all or some of the required quantity of sodium hypophosphite is introduced before the start of the polymerisation as a load in the tank bottom of the reactor.
4. A method of obtaining homopolymers and/or copolymers according to one of Claims 1 to 3, characterised in that the required quantity used of phosphorous acid and/or its salts or of sodium hypophosphite is greater than or equal to 0.5% by weight with respect to the total mass of the monomer or monomers.
5. A method of obtaining homopolymers and/or copolymers according to one of Claims 1 to 4, characterised in that the sodium hydroxide, potassium hydroxide or lithium hydroxide are

added in the form of a solution, in the form of a powder or in the form of pellets.

6. A method of obtaining homopolymers and/or copolymers according to one of Claims 1 to 4, characterised in that the calcium hydroxide, calcium oxide, magnesium hydroxide or magnesium oxide are added in the form of a suspension, in the form of a powder or in the form of the salts of the corresponding anionic monomers such as calcium acrylate or methacrylate or magnesium acrylate or methacrylate.

7. A method of obtaining homopolymers and/or copolymers according to one of Claims 1 to 6, characterised in that the ethylenically unsaturated monomer or monomers is or are chosen from amongst at least one of the ethylenically unsaturated anionic comonomers such as acrylic and/or methacrylic, itaconic, crotonic or fumaric acid, maleic anhydride or isocrotonic, aconitic, mesaconic, sinapinic, undecylenic or angelic acid, acrylamido methyl propanesulphonic acid or sodium methallylsulphonate and are optionally chosen from amongst the ethylenically unsaturated non-ionic comonomers such as acrylamide and/or methacrylamide, and preferentially chosen from amongst acrylic and/or methacrylic acid.

8. A method of obtaining homopolymers according to Claim 7, characterised in that the ethylenically unsaturated monomer is acrylic acid.

9. A polymer in aqueous solution obtained by the method according to any one of Claims 1 to 8, characterised in that the degree of neutralisation of the active acid sites is between 40% and 90%, limits included, for the sodium, potassium or lithium ions and between 10% and 60%, limits included, for the calcium and magnesium ions.

10. A polymer in aqueous solution according to Claim 9, characterised in that it is in the completely neutralised form.
11. A polymer in aqueous solution according to Claim 9, characterised in that it is partially neutralised.
12. A polymer in aqueous solution according to any one of Claims 9 to 11, characterised in that it has a molecular weight in M_w weight of between 2000 and 16,000, preferentially between 3500 and 6500, determined by aqueous GPC whose standards, used as references, belong to a series of sodium polyacrylates sold by the company Polymer Standards Service under the names PSS-PAA varying from 18K to 2K.
13. Use of the polymer in aqueous solution according to one of Claims 9 to 12 as a grinding-aid agent and/or as a dispersing agent of mineral materials in an aqueous medium.
14. Use of the polymer in aqueous solution according to one of Claims 9 to 12 as water retaining agent in the paper making industry.
15. Use of the polymer in aqueous solution as claimed in any one of claims 9 to 12 as an agent for sequestering or inhibiting precipitation and/or mineral incrustations in the treatment of industrial and/or domestic waters.
16. Use of the polymer in aqueous solution as claimed in any one of claims 9 to 12 as an anti-scale and anti-corrosion agent in the field of inverse osmosis and ultra-filtration.
17. Use of the polymer in aqueous solution as claimed in any one of claims 9 to 12 as a thinning agent for drilling fluids.
18. Use of the polymer in aqueous solution as claimed in any

one of claims 9 to 12 in the field of detergents as an anti-scale and dispersing agent which does not destabilise the chlorometric rate of the hypochlorites present in the detergent formulae or as a stabilising agent for zeolites or as a builder or co-builder.

19. Aqueous suspensions of mineral materials containing the polymer according to any one of Claims 9 to 12.

20. Use of aqueous suspensions of mineral materials according to Claim 19 in the field of paper, paint, ceramics, drilling fluids and detergents.

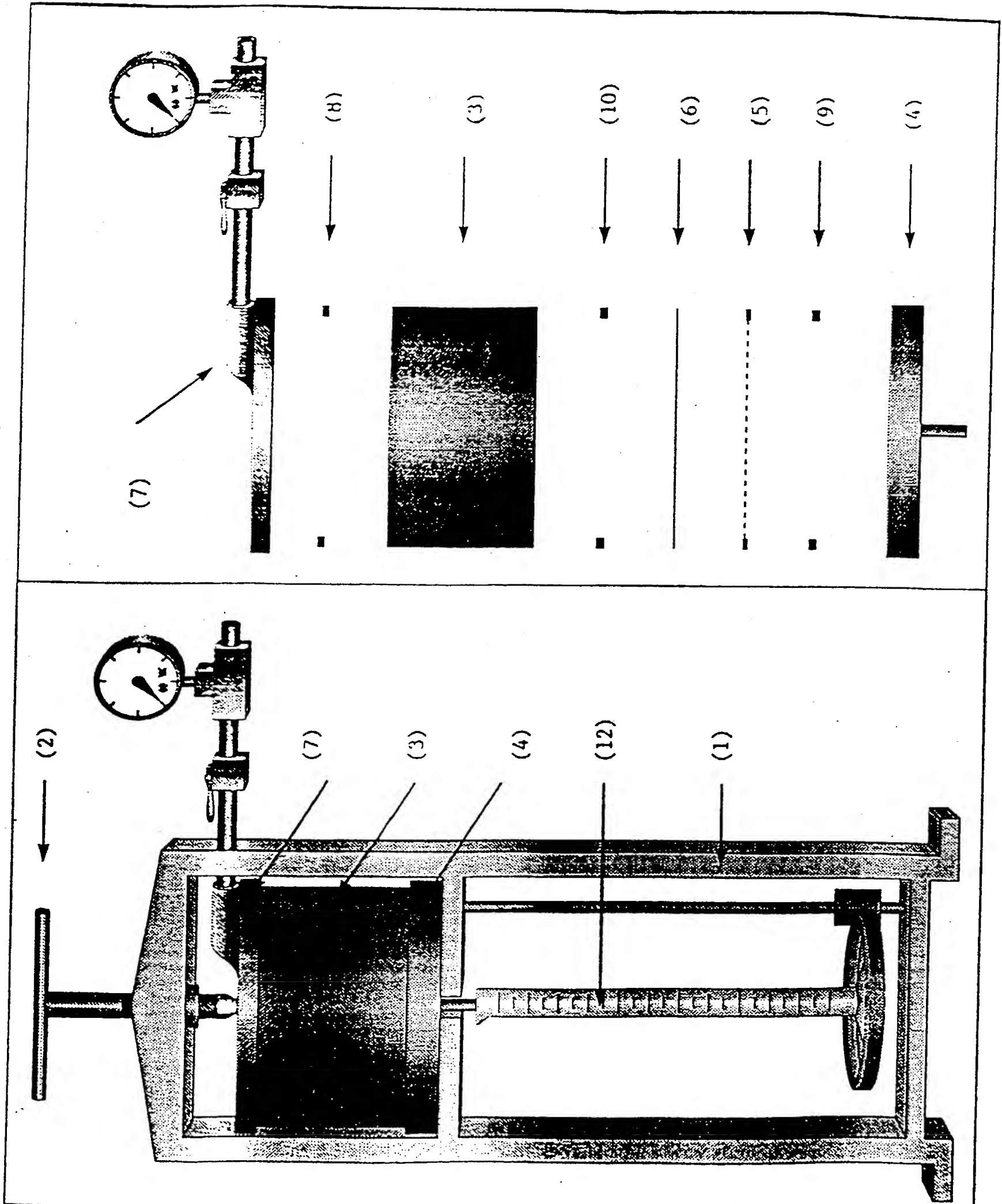
ABSTRACT

A method of obtaining homopolymers and/or copolymers in aqueous solution by the use of phosphorous acid and/or its salts or sodium hypophosphite and by neutralisation during the polymerisation of the ethylenically unsaturated monomers by the continuous addition, first of all, of bases such as sodium hydroxide, potassium hydroxide or lithium hydroxide and then bases of alkaline earths such as calcium hydroxide, magnesium hydroxide, calcium oxide or magnesium oxide.

The polymers obtained by the said method and uses thereof.

PLANCHE 1/1

FIGURE 1



Declaration and Power of Attorney for Patent Application

Déclaration et Pouvoirs pour Demande de Brevet

French Language Declaration

En tant l'inventeur nommé ci-après, je déclare par le présent acte que:

Mon domicile, mon adresse postale et ma nationalité sont ceux figurant ci-dessous à côté de mon nom.

Je crois être le premier inventeur original et unique (si un seul nom est mentionné ci-dessous), ou l'un des premiers co-inventeurs originaux (si plusieurs noms sont mentionnés ci-dessous) de l'objet revendiqué, pour lequel une demande de brevet a été déposée concernant l'invention intitulée

et dont la description est fournie ci-joint à moins

☐ ci-joint

☐ a été déposée le _____

sous le numéro de demande des Etats-Unis ou le numéro de demande international PCT

_____ et modifiée le

_____ (le cas échéant).

Je déclare par le présent acte avoir passé en revue et compris le contenu de la description ci-dessus, revendications comprises, telles que modifiées par toute modification dont il aura été fait référence ci-dessus.

Je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations.

As a below named inventor, I hereby declare that:

My residence, mailing address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

METHOD FOR OBTAINING WATER SOLUBLE POLYMERS, RESULTING POLYMERS AND USES THEREOF (as amended)

the specification of which

☐ is attached hereto.

☒ was filed on March 18, 2002

as United States Application Number or PCT International Application Number

10/070,424 and was amended on

_____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

French Language Declaration

Je revendique par le présent acte avoir la priorité étrangère, en vertu du Titre 35, § 119(a)-(d) ou § 365(b) du Code des Etats-Unis, sur toute demande étrangère de brevet ou certificat d'inventeur ou, en vertu du Titre 35, § 365(a) du même Code, sur toute demande internationale PCT désignant au moins un pays autre que les Etats-Unis et figurant ci-dessous et, en cochant la case, j'ai aussi indiqué ci-dessous toute demande étrangère de brevet, tout certificat d'inventeur ou toute demande internationale PCT ayant une date de dépôt précédant celle de la demande à propos de laquelle une priorité est revendiquée.

Prior Foreign Application(s)

Demande(s) de brevet antérieure(s) dans un autre pays.

99/11798

(Number)
(Numéro)

France

(Country)
(Pays)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 119(e) du Code des Etats-Unis, de toute demande de brevet provisoire effectuée aux Etats-Unis et figurant ci-dessous.

(Application No.)
(N° de demande)

(Filing Date)
(Date de dépôt)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 120 du Code des Etats-Unis, de toute demande de brevet effectuée aux Etats-Unis, ou en vertu du Titre 35, § 365(c) du même Code, de toute demande internationale PCT désignant les Etats-Unis et figurant ci-dessous et, dans la mesure où l'objet de chacune des revendications de cette demande de brevet n'est pas divulgué dans la demande antérieure américaine ou internationale PCT, en vertu des dispositions du premier paragraphe du Titre 35, § 112 du Code des Etats-Unis, je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations, dont j'ai pu disposer entre la date de dépôt de la demande antérieure et la date de dépôt de la demande nationale ou internationale PCT de la présente demande:

PCT/FR00/02519

(Application No.)
(N° de demande)

September 13, 2000

(Filing Date)
(Date de dépôt)

(Application No.)
(N° de demande)

(Filing Date)
(Date de dépôt)

Je déclare par le présent acte que toute déclaration ci-incluse est, à ma connaissance, véridique et que toute déclaration formulée à partir de renseignements ou de suppositions est tenue pour véridique; et de plus, que toutes ces déclarations ont été formulées en sachant que toute fausse déclaration volontaire ou son équivalent est passible d'une amende ou d'une incarcération, ou des deux, en vertu de la § 1001 du Titre 18 du Code des Etats-Unis, et que de telles déclarations volontairement fausses risquent de compromettre la validité de la demande de brevet ou du brevet délivré à partir de celle-ci.

I hereby claim foreign priority under Title 35, United States Code, § 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Claimed
Droit de priorité
Revendiqué

16 September 1999

(Day/Month/Year Filed)
(Jour/Mois/Année de dépôt)

☒
Yes
Oui

☐
No
Non

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

(Application No.)
(N° de demande)

(Filing Date)
(Date de dépôt)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Status: Patented, Pending, Abandoned)
(Statut : breveté, en cours d'examen, abandonné)

(Status: Patented, Pending, Abandoned)
(Statut : breveté, en cours d'examen, abandonné)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

French Language Declaration

POUVOIRS: En tant que l'inventeur cité, je désigne par la présente l'(les) avocat(s) suivant(s) pour qu'ils poursuive(nt) la procédure de cette demande de brevet et traite(nt) toute affaire s'y rapportant avec l'Office des brevets et des marques: (*mentionner le nom et le numéro d'enregistrement*).

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)



022850

Addresser toute correspondance à:

Send Correspondence to:



022850

Adresser tout appel téléphonique à:
(nom et numéro de téléphone)

Direct Telephone calls to: (name and telephone number)

(703) 413-3000

Nom complete de l'unique ou premier inventeur	Full name of sole or first inventor <u>Jean-Marc SUAU</u>
Signature de l'inventeur	Inventor's signature
Date	Date <u>April 09, 2002</u>
Domicile	Residence <u>Le Perrault, F-69480 Lucenay, FRANCE</u>
Nationalité	Citizenship <u>France</u>
Adresse Postale	Mailing Address <u>Same as Above</u>

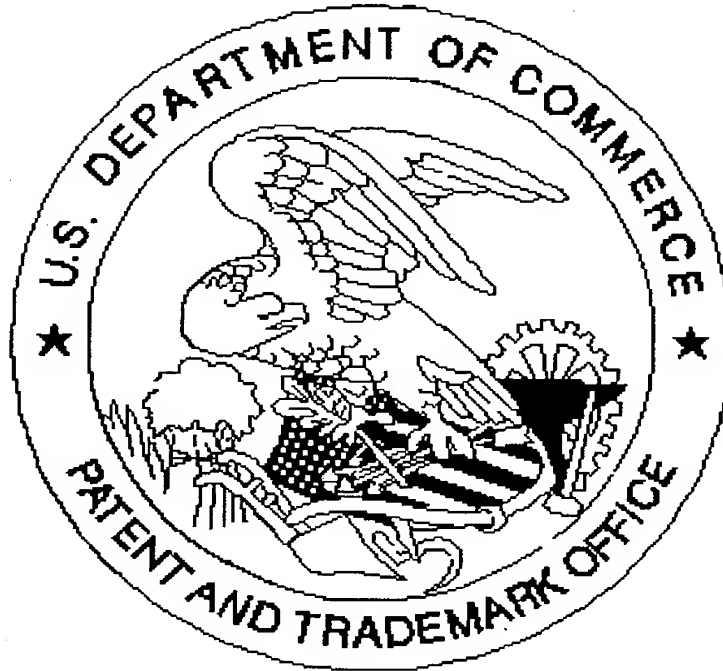
Nom complete du second co-inventeur, le cas echean	Full name of second joint inventor, If any <u>Christian JACQUEMET</u>
Signature de l'inventeur	Second inventor's signature
Datum	Date <u>April 09, 2002</u>
Domicile	Residence <u>24, allée Henriette, F-69005 Lyon, FRANCE</u>
Nationalité	Citizenship <u>France</u>
Adresse Postale	Mailing Address <u>Same as Above</u>

French Language Declaration

Nom complet du troisième co-inventeur, le cas échéant	Full name of third joint inventor, if any Jean-Bernard EGRAZ
Signature de l'inventeur	Third inventor's signature
Date	Date April 09, 2002
Domicile	Residence Impasse du Moulin Carron, F-69130 Ecully, FRANCE
Nationalité	Citizenship France
Adresse Postale	Mailing Address Same as Above

Nom complet du quatrième co-inventeur, le cas échéant	Full name of fourth joint inventor, if any Jacques MONGOIN
Signature de l'inventeur	Fourth inventor's signature
Date	Date April 16, 2002
Domicile	Residence Enchuel, F-69550 Quincieux, FRANCE
Nationalité	Citizenship France
Adresse Postale	Mailing Address Same as Above

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☒ *Scanned copy is best available. Figure 1, is dark.*